

# TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 48876

**DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/646183

INTERNATIONAL APPLICATION NO.  
PCT/EP 99/01794

**INTERNATIONAL FILING DATE**  
**18 March 1999**

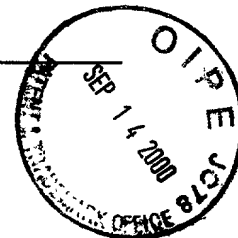
PRIORITY DATE CLAIMED  
20 March 1998

**TITLE OF INVENTION: INHERENTLY LIGHT- AND HEAT-STABILIZED POLYAMIDES OF IMPROVED WETFASTNESS**

APPLICANT(S) FOR DO/EOUS Ulrike BREINER, Manfred JULIUS, Rainer NEUBERG, Robert WEISS, Axel WILMS,  
Harry Y. HU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. /X/ This express request to begin national examination procedures (35 U.S.C.371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
- a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
- b./ / has been transmitted by the International Bureau.
- c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. /X/ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
- a./X/ are transmitted herewith (required only if not transmitted by the International Bureau).
- b./ / have been transmitted by the International Bureau.
- c./ / have not been made; however, the time limit for making such amendments has NOT expired.
- d./ / have not been made and will not be made.
8. /X/ A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
9. / X/ An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).
- 10./ / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
- 11./X / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
- 12./ X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
- 13./X / A FIRST preliminary amendment.
- / / A SECOND or SUBSEQUENT preliminary amendment.
- 14./ / A substitute specification.
- 15./ / A change of power of attorney and/or address letter.
- 16./x / Other items or information.  
International Search Report  
International Preliminary Examination Report

[illegible]

09/646183

U.S. Appl. No. (If Known) INTERNATIONAL APPLN. NO.  
PCT/EP 99/01794ATTORNEY'S DOCKET NO.  
48876

		CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted			
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the EPO or JPO.....	\$840.00	840.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$750.00			
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....\$700.00			
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....\$ 970.00			
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....\$96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT = \$		840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(e)).			
Claims	Number Filed	Number Extra	Rate
Total Claims	13 -20		X\$18.
Indep. Claims	1 -3		X\$78.
Multiple dependent claim(s) (if applicable)		+270.	
TOTAL OF ABOVE CALCULATION		=	840.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			
SUBTOTAL		=	840.00
Processing fee of \$130. for furnishing the English translation later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +			
TOTAL NATIONAL FEE		=	840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property =			
TOTAL FEES ENCLOSED		= \$	880.00
		Amount to be refunded: \$	
		Charged \$	

a./X/ A check in the amount of \$ 880. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

KEIL & WEINKAUF  
1101 Connecticut Ave., N.W.  
Washington, D. C. 20036

SIGNATURE

Herbert B. Keil

NAME

Registration No. 18,967

09/646183

422 Rec'd PCT/PTO 14 SEP 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of )  
BREINER et al. ) BOX PCT

International Application )  
PCT/EP 99/01794 )

Filed: March 18, 1999 )

For: INHERENTLY LIGHT- AND HEAT-STABILIZED POLYAMIDES OF  
IMPROVED WETFASTNESS

PRELIMINARY AMENDMENT

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Claim 3, line 1, delete "or 2".

Claim 4, line 1, delete "any of claims 1 to 3" and insert --claim 1--.

Claim 5, line 1, delete "any of claims 1 to 4" and insert --claim 1--.

Claim 6, line 1, delete "any of claims 1 to 5" and insert --claim 1--.

Claim 7, line 1, delete "any of claims 1 to 6" and insert --claim 1--.

Claim 8, line 1, delete "any of claims 1 to 2" and insert --claim 1--.

Claim 9, line 1, delete "any of claims 1 to 8" and insert --claim 1--.

Claim 10, lines 1 and 2, delete "any of claims 1 to 9" and insert --claim 1--.

Claim 11, lines 1 and 2, delete "any of claims 1 to 9" and insert --claim 1--.

REMARKS

The claims were amended in the preliminary examination. The claims have been amended further to eliminate multiple dependency and to put it in better form for U.S. filing. No new matter is included.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

A handwritten signature in dark ink, appearing to read 'H B Keil', written over the firm name.

Herbert B. Keil  
Reg. No. 18,967

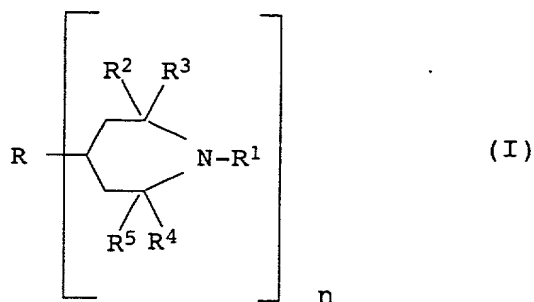
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(202)659-0100

422 Rec'd PCT/PTO 14 SEP 2000

Inherently light- and heat-stabilized polyamides of improved wetfastness

5 Specification

The present invention relates to a process for preparing polyamides, which comprises polymerizing starting monomers or starting oligomers in the presence of at least one compound of  
10 the formula (I)



25 where

R is a functional group R<sup>8</sup> which bears 1-4 identical or different amide-forming groups R<sup>7</sup>,  
30 R<sup>1</sup> is H, C<sub>1</sub>-C<sub>20</sub>-alkyl, cycloalkyl, benzyl or OR<sup>6</sup>, where  
R<sup>6</sup> is H, C<sub>1</sub>-C<sub>20</sub>-alkyl, cycloalkyl or benzyl,  
R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are independently C<sub>1</sub>-C<sub>10</sub>-alkyl,  
n is a natural number greater than 1, and

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the piperidine derivatives attached to R are identical or different with regard to the substituents, meaning R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>.

40 It further relates to polyamides obtainable by this process, to the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and moldings, and to filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide.

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00460-2297360

## 2

The preparation of polyamides, including nylon-6 and nylon-6,6, by addition or condensation polymerization from appropriate starting monomers or starting oligomers is common knowledge (Adolf Echte, Handbuch der technischen Polymerchemie, VCH Weinheim, 1993, p. 553).

The application properties of such polyamides, such as heat stability, light stability, dyeability, resistance to the washing out of color (color wetfastness), are unsatisfactory for many applications.

For instance, coloration problems can arise as a result of chemical changes (oxidative/thermal damage) to the polymer during carpet yarn or textile fabric heat setting. Both continuous filaments and staple fibers can be affected.

It is known to add stabilizers to the polyamide to improve these properties. Such an addition can take place before, during or after the polymerization, for example during the processing.

If the stabilizers are mixed into the polyamide and not attached to the polymer chain, they can migrate, evaporate or wash out of the polymer, so that the effectiveness of the stabilization decreases in an undesirable manner and the surroundings (air, dyebath, cleaning baths) may become contaminated. For instance, DE-A-39 01 717 describes improving the dyeability of polyamides by adding small amounts of at least one amino or imino compound having a cycloalkyl, aryl or hetaryl moiety in the molecule.

The addition of 2,2,6,6-tetramethylpiperidine derivatives with an amide-forming group in position 4 and with or without substitution in position 1 during the polymerization is described for example in WO 95/28443, DE-A-44 13 177, WO 97/05189 and WO 97/13800. The use of these stabilizers leads to a reduction in the rate of polymerization and hence to higher manufacturing costs for the polyamides due to a reduced space-time yield. In addition, the wetfastness of such polyamides is unsatisfactory.

It is an object of the present invention to provide a process for preparing polyamides, polyamides obtainable by this process, the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and moldings, and also filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide without the disadvantages mentioned.

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## 3

We have found that this object is achieved by the process for preparing polyamides defined at the beginning, polyamides obtainable by this process, the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and moldings, and also filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide.

Polyamides are herein to be understood as being homopolymers, copolymers, blends and grafts of synthetic long-chain polyamides having recurring amide groups in the polymer main chain as an essential constituent. Examples of such polyamides are nylon-6 (polycaprolactam), nylon-6,6 (polyhexamethylenedipamide), nylon-4,6 (polytetramethylenedipamide), nylon-6,10 (polyhexamethylene-sebacamide), nylon-7 (polyanthranilactam), nylon-11 (polyundecanolactam), nylon-12 (polydodecanolactam). As well as polyamides known by the generic name of nylon, polyamides further include the so-called aramids (aromatic polyamides), such as poly-meta-phenylene-isophthalamide (NOMEX<sup>®</sup> fiber, US-A-3,287,324) or poly-para-phenylene-terephthalamide (KEVLAR<sup>®</sup> fiber, US-A-3,671,542).

Polyamides can in principle be prepared by two methods.

In a polymerization from dicarboxylic acids and diamines and also in a polymerization from amino acids, the amino and carboxyl end groups of the starting monomers or starting oligomers react with one another to form an amide group and water. The water can subsequently be removed from the polymer. In a polymerization from carboxamides, the amino and amide end groups of the starting monomers or starting oligomers react with one another to form an amide group and ammonia. The ammonia can subsequently be removed from the polymer. This form of polymerization is customarily known as a condensation polymerization or polycondensation.

A polymerization from lactams as starting monomers or starting oligomers is customarily known as an addition polymerization.

Suitable starting monomers or starting oligomers for preparing polyamides are for example:

monomers or oligomers of C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>3</sub> to C<sub>18</sub>, amino acids, such as 6-aminocaproic acid, 11-aminoundecanoic acid, and also their dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of C<sub>2</sub> to C<sub>20</sub> amino acid amides, such as 6-aminocaproamide, 11-aminoundecanoamide, and also their dimers, trimers, tetramers, pentamers or hexamers,

- 5 monomers or oligomers of a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>12</sub>, alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,

with a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>14</sub>, aliphatic dicarboxylic  
10 acid, such as sebacic acid, decanedicarboxylic acid or adipic acid,

and also dimers, trimers, tetramers, pentamers or hexamers thereof,

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monomers or oligomers of a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>12</sub>, alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,

- 20 with a C<sub>8</sub> to C<sub>20</sub>, preferably C<sub>8</sub> to C<sub>12</sub>, aromatic dicarboxylic acid or its derivatives, for example chlorides, such as 2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid,

- 25 and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>12</sub>, alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,

30

with a C<sub>9</sub> to C<sub>20</sub>, preferably C<sub>9</sub> to C<sub>18</sub>, arylaliphatic dicarboxylic acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

- 35 and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>6</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>10</sub>, aromatic diamine, such as m- or p-phenylenediamine,

- 40 with a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>14</sub>, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid or adipic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

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monomers or oligomers of a C<sub>6</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>10</sub>, aromatic diamine, such as m- or p-phenylenediamine,

with a C<sub>8</sub> to C<sub>20</sub>, preferably C<sub>8</sub> to C<sub>12</sub>, aromatic dicarboxylic acid  
5 or its derivatives, for example chlorides, such as  
2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or  
terephthalic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>6</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>10</sub>, aromatic diamine, such as m- or p-phenylenediamine,

with a C<sub>9</sub> to C<sub>20</sub>, preferably C<sub>9</sub> to C<sub>18</sub>, arylaliphatic dicarboxylic acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

20 monomers or oligomers of a C<sub>7</sub> to C<sub>20</sub>, preferably C<sub>8</sub> to C<sub>18</sub>, aryl-aliphatic diamine, such as m- or p-xylylenediamine,

with a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>14</sub>, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid or adipic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>7</sub> to C<sub>20</sub>, preferably C<sub>8</sub> to C<sub>18</sub>, aryl-  
30 aliphatic diamine, such as m- or p-xylylenediamine,

with a C<sub>6</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>10</sub>, aromatic dicarboxylic acid or its derivatives, for example chlorides, such as 2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>7</sub> to C<sub>20</sub>, preferably C<sub>8</sub> to C<sub>18</sub>, aryl-  
40 aliphatic diamine, such as m- or p-xylylenediamine,

with a C<sub>9</sub> to C<sub>20</sub>, preferably C<sub>9</sub> to C<sub>18</sub>, arylaliphatic dicarboxylic acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

45 and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C<sub>2</sub> to C<sub>20</sub>, preferably C<sub>2</sub> to C<sub>18</sub>, aryl-aliphatic or preferably aliphatic lactam, such as enantholactam, undecanolactam, dodecanolactam or caprolactam,

- 5 and also homopolymers, copolymers, blends and grafts of such starting polymers or starting oligomers.

Preference is given here to those starting monomers or starting oligomers which polymerize to form the polyamides nylon-6,  
10 nylon-6,6, nylon-4,6, nylon-6,10, nylon-7, nylon-11, nylon-12 and the aramids poly(meta-phenyleneisophthalamide) or poly(para-phenyleneterephthalamide), especially nylon-6 and nylon-6,6.

In the compound of the formula (I), R is a functional group  
15 bearing 1-4 identical or different amide-forming groups R<sup>7</sup>.

R is suitably a C<sub>1</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>18</sub>, aromatic, preferably aliphatic unsaturated, preferably saturated, hydrocarbon R<sup>8</sup> bearing the 1-4 amide-forming groups R<sup>7</sup>.

20 The hydrocarbons R<sup>8</sup> can bear functional groups, such as ether groups, non-amide-forming amine groups or acid groups, such as phosphonic acid, phosphoric acid, preferably sulfonic acid groups or their derivatives, preferably salts, especially alkali metal  
25 salts, such as lithium, sodium or potassium salts.

In a preferred embodiment of the process of the present invention, R<sup>8</sup> is C<sub>1</sub>-C<sub>20</sub>-alkylene, especially hexamethylene, having no further functional groups apart from R<sup>7</sup>.

30 The amide-forming group R<sup>7</sup> can be selected from -(NHR<sup>9</sup>), where R<sup>9</sup> is H, alkyl having from 1 to 8 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms or alkylene having from 2 to 20 carbon atoms, carboxyl, a carboxyl derivative group or preferably  
35 -(NH)-. If R bears a plurality of groups R<sup>7</sup>, these groups can be different or preferably identical.

R<sup>1</sup> is suitably alkyl having from 1 to 20, preferably from 1 to 18, carbon atoms, a substituted or preferably unsubstituted benzyl  
40 group or a group OR<sup>6</sup>, where R<sup>6</sup> is an alkyl group having from 1 to 20, preferably from 1 to 18 carbon atoms, a substituted or preferably unsubstituted benzyl group or preferably hydrogen. R<sup>1</sup> is particularly preferably hydrogen.

Suitable radicals  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently alkyl having from 1 to 10 carbon atoms, preferably methyl or ethyl, especially methyl.  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  can be different or preferably identical.

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The index  $n$  can be a natural number greater than 1, such as 2, 3, 4, 5 or 6, preferably 2, 3 or 4, especially 2.

The piperidine derivatives attached to  $R$  can be identical or

10 different, preferably identical.

Compound (I) can be a single chemical compound or a mixture of different compounds.

15 A particularly preferred compound of the formula (I) is 1,6-bis-(4-amino-2,2,6,6-tetramethylpiperidino)hexane. This compound and its preparation are common knowledge and it is commercially available for example from Aldrich Chemical Company, Inc.

20 The compound of the formula (I) is added to the starting monomers or to the polymerizing reaction mixture and becomes attached to the polyamide through reaction of at least one of the amide-forming groups  $R^7$ . The secondary amino groups of the piperidine ring systems do not react because of steric hindrance.

25

By chemically attaching the compound (I) to or within a polyamide, the process of the present invention provides polyamides having the advantageous properties mentioned at the beginning. The process of the present invention thus offers the

30 advantage of obviating the separate step otherwise necessary to improve the properties of pure polyamides by admixture of compounds. This eliminates problems or quality reductions as can arise on incorporation of such compounds following surface application to the polymer granules as a result of

35 incompatibility, viscosity degradation, migration, vaporization or washoff of these compounds or stresses as occur with compounding.

The polymerization of the starting monomers in the presence of

40 the compound (I) is preferably carried out according to customary processes. For instance, the polymerization of caprolactam in the presence of a compound (I) can be carried out for example according to the continuous or batchwise processes described in DE-A 14 95 198, DE-A 25 58 480, DE-A 44 13 177, Polymerization Processes, Interscience, New York, 1977, p. 424-467 and Handbuch der Technischen Polymerchemie, VCH Verlagsgesellschaft, Weinheim, 1993, p. 546-554. The polymerization of 66 salt in the presence

of a compound (I) can be carried out by the customary batchwise process (see: Polymerization Processes, Interscience, New York, 1977, p. 424-467, especially 444-446) or by a continuous process, for example as described in EP-A 129 196. In principle, compound 5 (I) and the starting monomers can be introduced into the reactor separately or as a mixture. The compound (I) is preferably added according to a predetermined amount/time program.

In a preferred embodiment, the compound (I) is added to the 10 starting monomers in an amount of from 0.015 to 0.4 mol%, preferably from 0.025 to 0.25 mol%, based on 1 mol of amide groups of the polyamide. This amount is based for example on 1 mol of caprolactam when nylon-6 is to be prepared or on 0.5 mol of 66 salt when nylon-6,6 is to be prepared.

15 In a preferred embodiment of the invention, the compound (I) is combined with at least one of the customary chain regulators. Examples of suitable chain regulators are aliphatic and aromatic monocarboxylic acids such as acetic acid, propionic acid and 20 benzoic acid, aliphatic and aromatic dicarboxylic acids such as C<sub>4</sub>-C<sub>10</sub>-alkanedicarboxylic acids, preferably sebacic acid and dodecanedioic acid, especially adipic acid and azelaic acid, aliphatic C<sub>5</sub>-C<sub>8</sub>-cycloalkanedicarboxylic acids, especially cyclohexane-1,4-dicarboxylic acid, aromatic dicarboxylic acids 25 such as benzene- and naphthalene-dicarboxylic acids, preferably isophthalic acid, 2,6-naphthalenedicarboxylic acid, especially terephthalic acid, monofunctional amines and bifunctional amines, preferably hexamethylenediamine or cyclohexyldiamine and also mixtures of such acids and mixtures of such amines. The chain 30 regulator combination and the amounts used are selected inter alia according to the desired polymer properties, such as viscosity or end group content. When dicarboxylic acids are used as chain regulators, it is preferable to use the chain regulator in an amount of from 0.06 to 0.6 mol%, preferably in an amount of 35 from 0.1 to 0.5 mol%, based on 1 mol of amide group of the polyamide.

In another preferred embodiment, the polymerization of the process of the present invention is carried out in the presence 40 of at least one pigment. Preferred pigments are titanium dioxide, preferably titanium dioxide in the anatase form, or color-conferring compounds which are organic or inorganic in character. The pigments are preferably added in an amount of from 0 to 5 parts by weight, especially in an amount from 0.02 to 2 parts by 45 weight, based on 100 parts by weight of polyamide. The pigments can be added to the reactor with the starting materials or separately therefrom. The use of a compound (I) (even as a chain

regulator constituent) considerably improves the properties of the polymer compared with a polymer incorporating only pigment and no compound (I) or only pigment and one of the 2,2,6,6-tetramethylpiperidine derivatives mentioned at the beginning.

The polyamides of the present invention are advantageously useful for preparing filaments, fibers, films, sheetlike structures and moldings. Filaments obtained from polyamides, especially polycaprolactam, by high speed spinning at takeoff speeds of at least 4000 m/min are particularly advantageous. The filaments, fibers, films, sheetlike structures and moldings obtained using the polyamides of the present invention have many uses, for example as textile apparel or carpet fibers.

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#### Examples

The relative viscosity of the polyamides was determined in 1% strength solution (1 g/100 ml) in concentrated sulfuric acid (96% by weight) at 25°C.

20

The end group content was determined by acidimetric titration. The amino end groups were titrated with perchloro [sic] acid in a solution in 70:30 (parts by weight) phenol/methanol. The carboxyl end groups were titrated with potassium hydroxide solution in a solution in benzyl alcohol.

25

To determine the color wetfastness, yarns were knitted up, then heat-set, dyed, treated with dye fixative and dried. The color fastness was determined in accordance with ISO-E01:1994 (water fastness, severe).

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The heat setting was carried out in a tenter at 196°C for 45 sec. The knit was then dyed in hot water (98°C) with a mixture of 2.53% by weight of Telon Fast Red AF3G 150% (corresponding to 3.8% of Acid Red 151) and 0.50% by weight of Acid Rhodamine B 400% (corresponding to 2% of Acid Red 52) at pH 3.5. To improve the dye fixation, the knit was treated for 30 min in a solution of 2% by weight of Mesitol NBS at 77°C in water and then rinsed out with water. After drying, the color fastness test was carried out. To this end, a sample of the fabric was moistened and placed between two pieces of undyed standard cloth. The three-ply stack was weighted with a standard weight and kept at 37°C for 4 h. The fastness was evaluated by comparing the depths of shade of the stained adjacent fabric with a standard gray scale.

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## 10

The UV stability of the yarns was determined in accordance with DIN 54004 (ISO 105 B 02) after 14 days' irradiation and subsequent measurement of the residual strength compared with an untreated sample.

5

To determine the heat-setting stability, a 5 g hank was aged for 120 sec in a thermal cabinet preheated to 185°C. Subsequently the breaking strength of the yarn was determined in comparison with an untreated yarn and reported as residual breaking strength [%].

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The condensation potential was determined from the product of condensation-capable amino end groups and carboxyl end groups.

Preparation of polyamides (a)

15

In a 360 l vessel, a mixture of 100 kg of caprolactam, 15 kg of water and the additives of Table 1 (reported quantities in % by weight based on caprolactam) was heated to 260°C in the course of 2 hours. After decompression over 90 min, the mixture was

20 postcondensed at 260°C for 45 min.

The product was then pelletized, divided into two portions and each being extracted three times with 100 l of water at 100°C in a 100 l vessel for 5 hours at a time, and dried in a tumble dryer

25 at 160°C under nitrogen.

The polymers were spun on a high speed spinning machine (Ems-Inventa AG) by the H4S process at 270°C and with a winding speed of 5040 m/min to 44 dtex 12 filament yarn of round cross section. The takeoff speed was 4300 m/min (duo 1), the draw ratio was 1 : 1.28 (duo 2 = 5500 m/min) and the yarn tension upstream of the winder was 3 cN. The steam box was operated with 3 bar process steam, and the spin finish content of the yarn was 0.8%. The yarns had the following properties: elongation 42%, tenacity

35 5.2 cN/dtex, boiling water shrinkage 14%.

The properties of the polyamides are summarized in Table 2. The polyamides of the present invention have improved light and heat stability and also improved wetfastness over the comparative

40 polyamides.

45

Table 1

Additive	Terephthalic acid	4-Amino-2,2,6,6-tetramethylpiperidine	1,6-bis(4-Amino-2,2,6,6-tetramethylpiperidino)hexane
Inventive Example 1	0.6	-/-	0.7
Inventive Example 2	0.6	-/-	0.5
Comparative Example 1	0.5	0.3	-/-

Table 2

Product	RV	AEG	CEG	CP	UV stab.	Heat-set. stab.	Color wetfastn.
Inv. 1	2.47	71	74	2945	79	90	4.4
Inv. 2	2.38	63	87	2440	74	75	3.7
Comp. 1	2.43	41	77	1925	73	73	3.6

RV	Relative viscosity
AEG	Amino end group content in meq/kg
5 CEG	Carboxyl end group content in meq/kg
KP	Condensation potential
UV stab.	UV stability, residual ultimate tensile strength in %
Heat-set. stab.	Heat-setting stability, residual tensile strength in %
10 Color wetfastn.	Wetfastness, AATCC gray scale

## Preparation of polyamides (b)

- 15 The mixtures of Table 3 were sealed in a glass tube under a nitrogen atmosphere. The sealed tube was heated to 260°C for the reaction times of Table 4. The products had the RV values of Table 4.

20 Table 3

	Inv. 3	Comp. 2
	50 g of caprolactam	50 g of caprolactam
25	0.285 g of terephthalic acid	0.285 g of terephthalic acid
	25 ml of water	25 ml of water
	0.140 g of 1,6-bis(4-amino-2,2,6,6-tetramethylpiperidino)hexane (0.2 mol% based on caprolactam)	0.354 g of 4-amino-2,2,6,6-tetramethylpiperidine (0.2 mol% based on caprolactam)

30 Table 4

	Reaction time [h]	Inv. 3, RV	Inv. 3, AEG	Comp. 2, RV	Comp. 2, AEG
35	0.5	1.20		1.24	
	1.5	1.78		1.81	
	3	1.98		2.01	
	6	1.99		2.08	
40	9	2.1	108	2.08	70

## Preparation of polyamides (c)

- A mixture as per Table 5 was [lacuna] to 270°C for 1 hour in a 1 liter autoclave. After decompression over 45 minutes, the mixture was postcondensed at 260°C for 60 minutes. The product was



13

then pelletized, extracted with water and dried at 80°C. The results of Table 6 were found.

Table 5

5

	Comp. 3	Comp. 4	Inv. 4
	300 g of caprolactam	300 g of caprolactam	300 g of caprolactam
	30 g of water	30 g of water	30 g of water
10	1.68 g of terephthalic acid	1.68 g of terephthalic acid	1.68 g of terephthalic acid
15	0.84 g of 4-amino-2,2,6,6-tetra- methylpiperidine (0.2 mol% based on caprolactam)	1.68 g of 4-amino-2,2,6,6-tetra- methylpiperidine (0.4 mol% based on caprolactam)	2.1 g of 1,6-bis(4-amino-2,2,6,6- tetramethylpiperidino)- hexane (0.2 mol% based on caprolactam)

20 Table 6

Comp. 3, RV	Comp. 4, RV	Inv. 4, RV
2.40	2.32	2.47

25 Doubling the regulator content on going from Comp. 3 to Comp. 4, i.e., doubling the number of sterically hindered amino groups in the polymer, slows down the growth in molecular weight and reduces the postcondensation potential of such products. The polymer of the present invention makes it possible to introduce

30 twice the number of sterically hindered amino end groups without reducing the postcondensation potential.

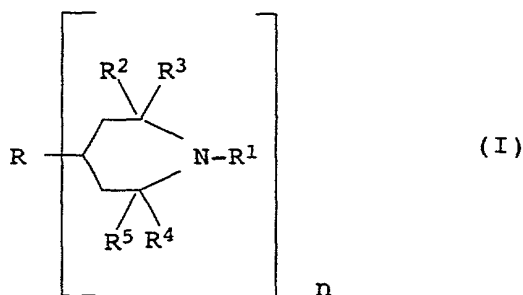
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We claim:

1. A process for preparing polyamides, which comprises  
 5 polymerizing starting monomers or starting oligomers in the presence of at least one compound of the formula (I)



20 R is a C<sub>1</sub>-C<sub>20</sub> aliphatic saturated hydrocarbon R<sup>8</sup> which bears 1-4 identical or different amide-forming groups R<sup>7</sup>,

25 R<sup>1</sup> is H, C<sub>1</sub>-C<sub>20</sub>-alkyl, cycloalkyl, benzyl or OR<sup>6</sup>, where

R<sup>6</sup> is H, C<sub>1</sub>-C<sub>20</sub>-alkyl, cycloalkyl or benzyl,

30 R<sup>7</sup> is selected from the group consisting of -(NHR<sup>9</sup>), carboxyl and carboxylic acid derivatives, R<sup>9</sup> being H, alkyl having from 1 to 8 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms or alkylene having from 2 to 20 carbon atoms,

R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are independently C<sub>1</sub>-C<sub>10</sub>-alkyl,

35 n is a natural number greater than 1,

the piperidine derivatives attached to R being identical or different with regard to the substituents, meaning R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>,

40 wherein the compound of the formula I is added to the starting monomers or to the polymerizing reaction mixture and becomes attached to the polyamide through reaction of at least one of the amide-forming groups R<sup>7</sup>.

45

## 15

2. A process as claimed in claim 1, wherein the piperidine derivatives attached to R are identical with regard to the substituents, meaning R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>.

- 5 3. A process as claimed in claim 1 or 2, wherein R<sup>1</sup> is H.

4. A process as claimed in any of claims 1 to 3, wherein the R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> substituents on any one piperidine derivative are identical.

10

5. A process as claimed in any of claims 1 to 4, wherein R<sup>2</sup> on any one piperidine derivative is methyl.

6. A process as claimed in any of claims 1 to 5, wherein n is 2.

15

7. A process as claimed in any of claims 1 to 6, wherein R is a group of the formula - NH - R<sup>8</sup> - NH - where R<sup>8</sup> is alkylene having from 1 to 20 carbon atoms.

- 20 8. A process as claimed in any of claims 1 to 2, wherein R is - NH - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - NH - .

9. A process as claimed in any of claims 1 to 8, wherein the polymerizing is carried out in the presence of at least one pigment.

25

10. The use of a compound (I) as set forth in any of claims 1 to 9 for preparing polyamides.

- 30 11. A polyamide obtainable by a process as claimed in any of claims 1 to 9.

12. The use of a polyamide as claimed in claim 11 for preparing filaments, fibers, films, sheetlike structures and moldings.

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13. Filaments, fibers, films, sheetlike structures and moldings comprising a polyamide as claimed in claim 11.

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Inherently light- and heat-stabilized polyamides of improved wetfastness

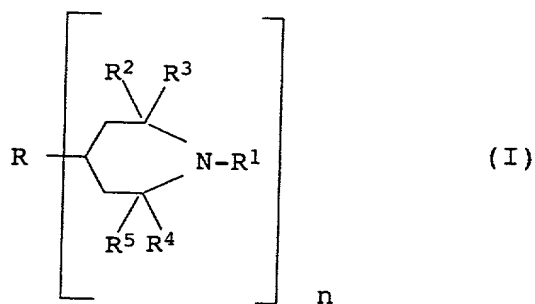
## 5 Abstract

A process for preparing polyamides comprises polymerizing starting monomers or starting oligomers in the presence of at least one compound of the formula (I)

10

15

20



where

25

R

is a functional group  $\text{R}^8$  which bears 1-4 identical or different amide-forming groups  $\text{R}^7$ ,

R<sup>1</sup>

30

is H,  $\text{C}_1\text{-C}_{20}$ -alkyl, cycloalkyl, benzyl or  $\text{OR}^6$ , where

R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>

$\text{R}^6$  is H,  $\text{C}_1\text{-C}_{20}$ -alkyl, cycloalkyl or benzyl, are independently  $\text{C}_1\text{-C}_{10}$ -alkyl,

n

is a natural number greater than 1, and

35 the piperidine derivatives attached to R are identical or different with regard to the substituents, meaning  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$ .

The polyamides are useful for preparing filaments, fibers, films,  
40 sheetlike structures and moldings.

45

# Declaration, Power of Attorney

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0050/048876

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Inherently light- and heat-stabilized polyamides of improved wetfastness

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP 99/01794

on 18/03/1999

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19812135.0	Germany	20 March 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

**Declaration**

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0050/048876

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

**Application Serial No.**

**Filing Date**

**Status (pending, patented,  
abandoned)**

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

2 And we (I) hereby appoint **Messrs. HERBERT. B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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